

THE SPATIAL DISTRIBUTION AND MINERALOGICAL ASSOCIATION OF ORGANICS IN THE TAGISH LAKE AND BELLS CARBONACEOUS CHONDRITES. S. J. Clemett¹, K. Nakamura-Messenger¹, K. L. Thomas-Keptra¹, S. Messenger² & D. S. McKay²; ¹ESCG Mail Code JE-23 / ²NASA Johnson Space Center, Houston, TX 77023 (e-mail: simon.j.clemett@nasa.gov).

Introduction: Chondritic meteorites represent some of the most primitive Solar System materials available for laboratory analysis. While the presence of simple organic molecules has been well documented in such materials [1], little is known about their spatial distribution and to what extent, if any, they exhibit specific mineralogical associations. This dichotomy arises since organic analysis typically involves solvent extraction as a preliminary step. To address these issues we have used two-step laser mass spectrometry (L^2MS) to map *in situ* the spatial distribution of aromatic and conjugated organics at the micron scale in freshly exposed surfaces of the Tagish Lake and Bells carbonaceous chondrites. Our specific goals are two-fold; firstly to investigate if and how abundance of organic species varies within the meteorite matrix both as an ensemble, and with respect to functional group (e.g., *R-OH* vs. *R-CH₃*) and between members of the same homologous series (e.g., *R-H* vs. *R-(CH₂)_nH*). Secondly, to determine whether observed spatial variations can be related to specific mineralogical and/or physical characteristics of the host matrix. In regard to the latter we are particularly interested in the role that carbonaceous nanoglobules [2] play as reservoirs of organic matter. Such globules, which are believed to have formed by photochemical processing of organic-rich ices in the presolar cold molecular cloud or the outermost reaches of the early protosolar disk, are abundant in both the Bells and Tagish Lake chondrites and are noteworthy for having particularly high enrichments in ²H and ¹⁵N [3,4].

Methods: Small chips, ~ 500 μm in diameter, of pristine Bells and Tagish Lake chondrites (carbonate-poor lithology) were separately embedded in epoxy (Embed 812™) on potted stubs and cross-sectioned using a diamond knife ultramicrotome. After cutting, the freshly exposed surfaces were imaged both optically and under UV illumination using a Nikon BX-50 fluorescent microscope equipped with a 330-385 nm excitation filter in combination with a 420 nm long-pass emission filter. We have previously found [5] that carbonaceous nanoglobules can be easily and non-destructively identified by their UV fluorescence (Fig. 1). Samples were then loaded, with no additional preparation, into our *ultra-L²MS* instrument. By spatially filtering the CO_2 laser beam used for surface desorption, our spot analysis resolution is $\lesssim 10 \mu\text{m}$. This can

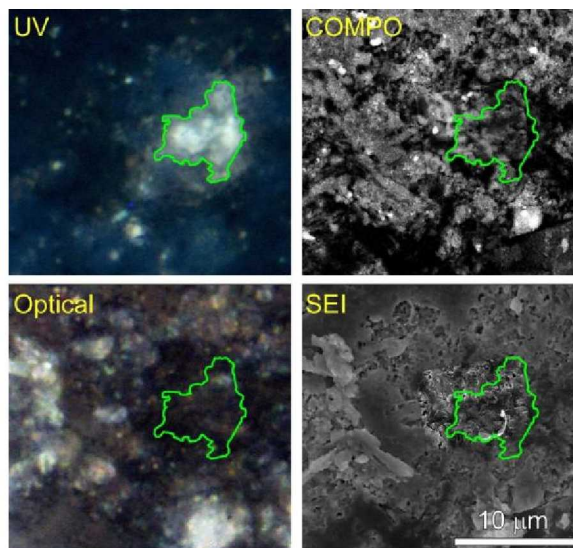


Figure 1: UV / Optical, and SEM backscatter (COMPO) / SEI images of a cluster of carbonaceous globules in fresh cut interior surface of Bells. UV fluorescence provides a simple non-destructive method to identify globule for subsequent analysis.

be further reduced by under stepping the sample stage translation during mapping which was achieved by rastering the sample stage under the desorption laser beam waist and acquiring single-shot mass spectra at 5 μm increments. By repeating this process and summing the successive spectra at each analysis point a complete mass spectra map of the surface can be produced. Each map typically covers a $\sim 500 \times 500 \mu\text{m}^2$ surface area and records all masses up to ~ 800 amu. Post- L^2MS samples were lightly *C*-coated for subsequent mineralogical and elemental analysis using a JEOL JSM-6340F field emission SEM equipped with EDX.

Results & Discussion: Averaging the spectra from mapped regions of both Bells and Tagish Lake (e.g., Fig. 2) shows that each chondrite matrix exhibits a suite of fused-ring aromatic species, their alkylated homologs and various monofunctionalized species. These spectra are consistent with the epoxy-free bulk matrix spectra obtained from crushing small fragments of each chondrite on to *Au*-foil. We note, however, there are several additional unusual mass peaks present in epoxy mounted samples that we have not previously observed, at any significant abundance, in other extra-terrestrial samples. In the Tagish Lake spectrum shown

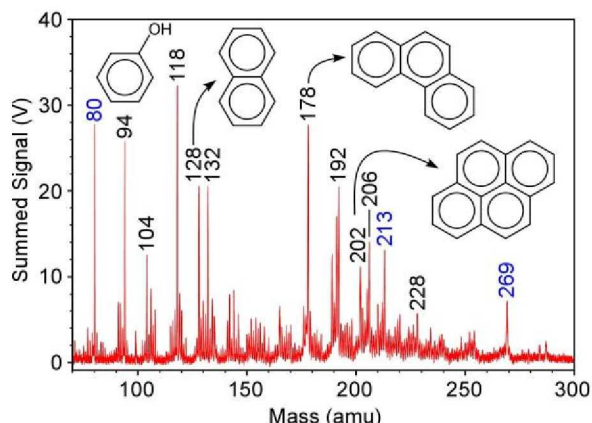


Figure 2: Summation of 4800 point spectra obtained from a $480 \times 480 \mu\text{m}^2$ surface of epoxy mounted Tagish Lake. Peaks labeled in blue represent secondary organics produced by reaction with epoxy during curing.

in Fig. 2 these peaks are labeled in blue and occur at 80, 213 and 269 amu. We believe these additional mass peaks represent secondary reaction products formed during curing of epoxy resin. As illustrated in Fig. 3 the cured epoxy mounting medium does not in and of itself, produce any spectra interferences since its cross-linked macromolecular structure prohibits desorption and hence detection by L^2MS . However during the curing process it is possible reagents present in the epoxy resin can react with indigenous matrix organics. One likely candidature is methyl-5-norbornene-2,3-dicarboxylic anhydride ($\text{C}_{10}\text{H}_{10}\text{O}_3$) that is used as a hardening agent for Embed 812™ epoxy resin, and is a powerful dehydrating agent that readily reacts with alcohols (R-OH) and 1°, 2°-amines (R-NH_2 & RR'-NH). Another possibility is the proprietary resin stabilizer which may contain pyrazene ($\text{C}_4\text{N}_2\text{H}_6$) derivatives.

Considering only those organics we previously identified in epoxy-free samples of Tagish Lake and Bells, we note the spatial distributions present in both chondrite matrixes, while heterogeneous, differ significantly. In Tagish Lake partitioning of functionally similar species such as the naphthalene (C_{10}H_8), phenanthrene ($\text{C}_{14}\text{H}_{10}$), and pyrene ($\text{C}_{16}\text{H}_{10}$) -- 2, 3 and 4-ring aromatics respectively -- is prevalent and occurs over ranges of tens-to-hundreds of microns. Such effects may reflect parent body geochromotagraphic separation by hydrothermal fluids during parent alteration [6]. In other cases, e.g., Fig. 3, different functional group species such as phenol ($\text{C}_6\text{H}_5\text{OH}$) are spatially anti-correlated. In contrast, the matrix of Bells is more complex with spatial heterogeneity tending to be reflected similarly in all species. We note at least a partial correlation between regions containing large clusters or concentrations of nanoglobules and increased abundance of organics. However, consistent with pre-

vious observations [5] it seems a more significant correlation relates to an increase of spectral complexity in the globule rich regions. This suggests that most of the organic matter associated with the globules is present as a bound polymeric or macromolecular assemblage. In Bells there also appears to be a distinct enrichment of organics associated with a relatively large sulphate-rich region present in one of the mapped surfaces that is consistent with anhydrite [7]. The origin of the anhydrite is uncertain and a terrestrial origin is possible [8].

Continuing studies are now focused on the use of S and or the thermal polymer CrystalBond™ as an embedding medium for microtoming. In the case of S an additional advantage is that it can be subsequently sublimed under vacuum prior to L^2MS analysis. We also plan to perform coordinated isotopic studies of mapped regions.

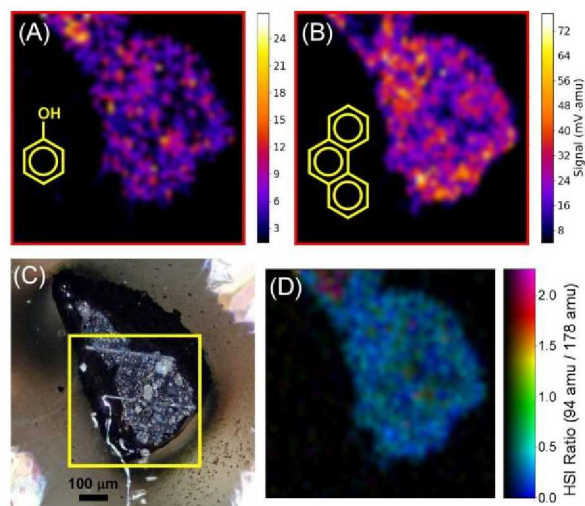


Figure 3: Spatial distribution maps of phenol (A) and phenanthrene (B) on a fresh cut interior surface of Tagish Lake. (C) Optical image of epoxy mounted sample with the mapped region show by the yellow box. The spatial correlation between difference organic species is most conveniently illustrated by image ratioing the phenol distribution with that for phenanthrene using an HSI color scheme (D). Note how the molecular distributions are both strongly heterogeneous and anti-correlated.

References: [1] Sephton M.A. (2002) *Nat. Prod. Rep.*, 19, 292-311. [2] Nakamura K. *et al.* (2002) *Int. J. Astrobiol.*, 1, 179-189. [3] Nakamura-Messenger K. *et al.* (2006) *Science*, 314, 1439-1442. [4] Messenger S. *et al.* (2008) *LPSC XXXIX*, Abst. #2391. [5] Clemett S.J. *et al.* (2009) *MAPS*, 44, A52. [6] Wing M.R. & Bada J.L. (1991) *GCA*, 55, 2937-2942. [7] Brearley A.J. (1995) *GCA*, 59, 2291-2317. [8] Gounelle G. & Zolensky M.E. (2001) *MAPS*, 36, 1321-1329.